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Transition metal free transfer hydrogenation of ketones promoted by 1,3-diarylimidazolium salts and KOH

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A B S T R A C T

An efficient transition metal free and greener catalytic system was developed for the selective transfer hydrogenation of saturated ketones to alcohols. This was achieved by the use of 1,3-diarylimidazolium salts in the presence of KOH as a promoter for the reaction. When the range of substrates was expanded to include unsaturated ketones, selective reduction of the double bond occurred. The catalyst efficiency was comparable to some established transition metal catalyzed systems. The current system utilizes mild aerobic reaction conditions compared to the inert atmosphere conditions required for the corresponding metal based systems.

Developing newer or improved methods for the catalytic reduction of ketones to alcohols is important because the end products have numerous applications in the pharmaceutical, perfumery, agrochemical, bulk and fine chemical industries.[1] Much of the work conducted to date on the catalytic transfer hydrogenation of ketones has utilized transition metals, such as platinum,[2] gold,[3] iridium,[4] rhodium[4c,5] and ruthenium.[6] Metal-based catalyst systems have been found to be very effective, although from a view point of sustainability they have many disadvantages. These include the fact that they are expensive and toxic to the environment, especially in the homogeneous environment in which they are most active.[7] Hence, there is a need for an inexpensive and environmentally friendly catalytic system capable of matching the activities of transition metal based systems.

Numerous applications of imidazolium salts exist in the literature.[8] Their use as precursors[9] towards the synthesis of *N*-heterocyclic carbene ligands (NHCs), which mimic, and in many instances have completely replaced phosphines[10] as ligands in organometallic reactions, has made them popular. The reasons for the superiority of NHCs over phosphines include their ease of preparation, relative air and moisture stability, low loading and high efficiency in catalysis.[11] Also, the ability of NHCs to be tuned sterically and electronically has been the driving force that has facilitated their use as ligands in metal complexes.[12] Thus, NHC-based complexes have been very effective in homogeneous catalysis and have found application in olefin metathesis,[13] hydroformylation,[14] hydrosilylation,[15] epoxidation[16] and hydrogenation reactions.[17] Most of these catalyzed reactions also require inert conditions, in addition to the use of heavy metals. Recently, Royo and co-workers,[18] in their search for less expensive and environmentally friendlier catalyst systems, synthesized iron(II) NHC complexes, which were found to be very effective catalysts for the transfer hydrogenation of ketones. However, the difficulties encountered in their synthesis,[19] which involved generation of reactive free carbenes prior to coordination, have greatly limited their use in catalysis.[20]

As part of an ongoing search to develop a cheaper, easily accessible, and a simple catalyst system, the imidazolium salts **1**–**4** (Fig. 1) were synthesized and used in a transition metal free system for the transfer hydrogenation of ketones. The 1,3-diarylimidazolium tetrafluoroborates with halides substituted at the *para*-position were synthesized according to a modified procedure.[9] It is also worth noting that the application of imidazolium-based ionic salts goes beyond their use as precursors to metal complexes;[21] they have even been applied widely in medicine as antimicrobial agents.[22] However, to our knowledge, their use in a transition metal free environment as organic catalysts for the activation of C=O and C=C bonds has not been explored.

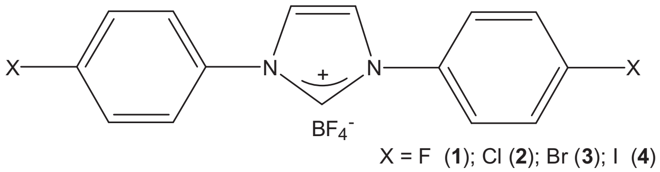

Figure 1. 1,3-Diarylimidazolium salts **1**–**4**.

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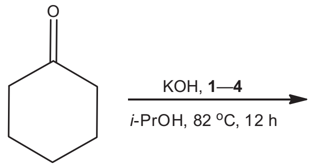
Table 1
Transfer hydrogenation of cyclohexanone catalyzed by imidazolium salts **1**–**4**



Imidazolium salt	Conversion[a] (%)	TON[b]
1	97	194
2	81	162
3	80	160
4	77	154

[a] Conversion was determined by GC analysis after 10 h for **1** and 12 h for **2**–**4**.
[b] Turnover number (TON) = mol product/mol catalyst.

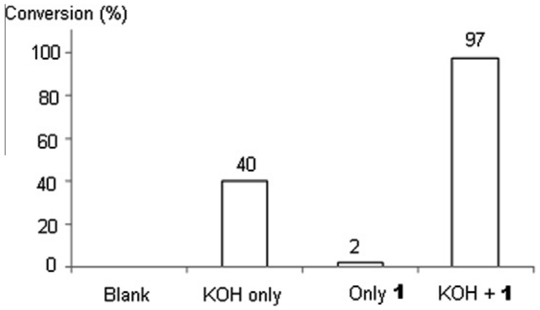
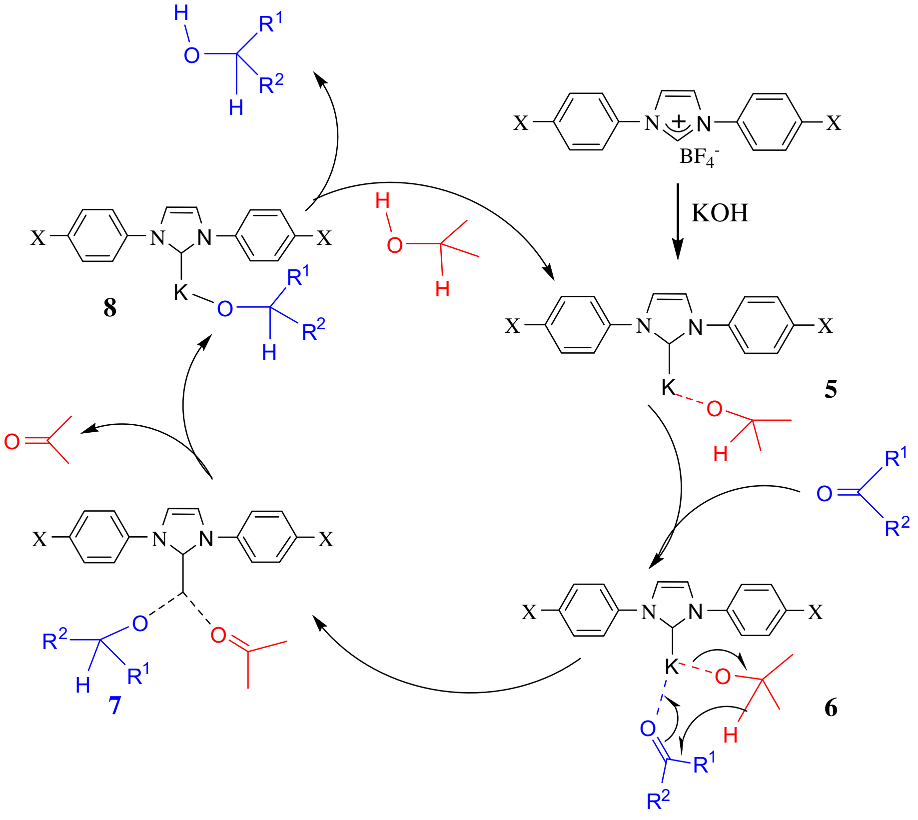


Figure 2. Relative conversions of cyclohexanone into cyclohexanol via transfer hydrogenation from isopropanol with key reagents (KOH and **1**).

The current study was inspired by our general interest in the incorporation of greener procedures in catalysis; hence transfer hydrogenation under metal-free conditions was investigated. In exploratory experiments, the transfer hydrogenation of cyclohexanone was examined with imidazolium salts **1**–**4** as the catalysts and isopropanol as the hydrogen source (and solvent) in a basic KOH environment. A typical experimental procedure for the transfer hydrogenation is described.[23,24] A very low catalyst loading of 0.5 mol % of the 1,3-diarylimidazolium salts (Fig. 1) was used in an aerobic environment and later in pure water, although very low conversion of the product was obtained in water. The salts **1–4** showed high activity toward the conversion of cyclohexanone into cyclohexanol with **1** showing the highest substrate conversion (Table 1). A turnover number (TON) up to 194 was observed which is higher than some of the metal-catalyzed reactions reported to date.[4a] This can be attributed to the negative inductive effect on the imidazolium carbon center due to the *para*-fluorine substituent. In general, the reactivity pattern can easily be attributed to the inductive effect which renders the imidazolium carbon more susceptible to attack by an electrophile such as the ketone C═O bond, or the alkene C═C bond (as observed for unsaturated ketones).

Moderate to high conversions of cyclohexanone into cyclohexanol were recorded as shown in Table 1. It was important from the onset to establish the role of the various components, notably the imidazolium salt, the KOH promoter and the solvent/hydrogen source in the catalytic transfer hydrogenation process. Evidence for the involvement of the carbene in facilitating reduction of the ketone was obtained from the results presented in Figure 2. When a blank run (no KOH or salt added) was conducted, there was no reaction observed, but when only KOH was added a 40% conversion of cyclohexanone into cyclohexanol was observed after 12 hours.



Scheme 1. Proposed mechanism for the transfer hydrogenation of ketones using 1,3-diarylimidazolium salts promoted by KOH in isopropanol.